

Pyridinolyses of 2,4-Dinitrophenyl Phenyl Carbonate and 2,4-Dinitrophenyl Benzoate: Effect of Nonleaving Group on Reactivity and Mechanism[†]

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Second-order rate constants (k_N) have been measured for reactions of 2,4-dinitrophenyl phenyl carbonate (**2**) with a series of pyridines in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C, and compared with the k_N values reported for the corresponding reactions of 2,4-dinitrophenyl benzoate (**1**) to investigate the effect of nonleaving group on reactivity and mechanism. The reactions of **2** result in larger k_N values than those of **1**. The Brønsted-type plot for the reactions of **2** exhibits a downward curvature (i.e., $\beta_2 = 0.84$ and $\beta_1 = 0.16$), which is typical for reactions reported to proceed through a stepwise mechanism with a change in rate-determining step. The pK_a at the center of the Brønsted curvature, defined as pK_a^0 , has been found to be 8.5 and 9.5 for the reactions of **2** and **1**, respectively. Dissection of k_N into the microscopic rate constants (e.g., k_1 and k_2/k_{-1} ratio) has revealed that the reactions of **2** result in larger k_1 values than those of **1**, indicating that PhO behaves as a stronger electron-withdrawing group than Ph. However, the k_2/k_{-1} ratio has been found to be independent of the electronic nature of Ph and PhO.

Key Words: Brønsted-type plot, 2,4-Dinitrophenyl phenyl carbonate, Pyridinolysis, Rate-determining step, Stepwise mechanism

Introduction

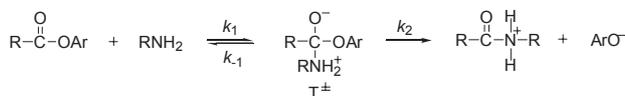
Aminolysis of esters has generally been reported to proceed through a stepwise mechanism with a zwitterionic tetrahedral intermediate (T^\pm) as shown in Scheme 1, in which the rate-determining step (RDS) is dependent on the basicity of the incoming amine and the leaving group.¹⁻¹⁴ The RDS has been suggested to change from breakdown of T^\pm to its formation as the basicity of the incoming amine increases.¹⁻¹⁴ Evidence provided for a change in RDS is curved Brønsted-type plots often observed for reactions of esters possessing a good leaving group (e.g., 2,4-dinitrophenoxide).¹⁻¹⁴

The pK_a at the center of the Brønsted curvature has been defined as pK_a^0 where a change in RDS occurs.⁸ It is now firmly understood that RDS changes from the k_2 step to the k_1 process as the incoming amine becomes more basic than the leaving group by 4 to 5 pK_a units or the leaving group becomes less basic than the amine. However, the effect of nonleaving group on pK_a^0 is controversial.⁸⁻¹⁴ Gresser and Jencks have found that the pK_a^0 in quinuclidinolysis of diaryl carbonates increases as the substituent in the nonleaving group of T^\pm changes from an electron-donating group (EDG) to an electron-withdrawing group (EWG), and concluded that an EWG increases pK_a^0 by decreasing the k_2/k_{-1} ratio.⁸ The explanation given is that an EWG in the nonleaving group could increase k_{-1} through the push provided the nonbonding electrons in the oxygen atom

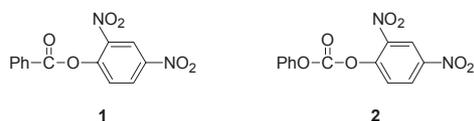
of the leaving aryloxy.⁸ A similar idea has been proposed for pyridinolysis of 2,4-dinitrophenyl X-substituted benzoates,⁹ aminolysis of *S*-2,4-dinitrophenyl X-substituted thiobenzoates,¹⁰ pyridinolysis of aryl dithiobenzoates and related esters,^{11a,b} and theoretical calculations on phenolysis of aryl acetates.^{11c}

In contrast, we have shown that the k_2/k_{-1} ratio is independent of the electronic nature of the substituent X in the nonleaving group for aminolysis of 2,4-dinitrophenyl X-substituted benzenesulfonates¹² and related compounds.^{13,14} We have proposed that expulsion of the nucleofuges from T^\pm would be retarded by an EWG but accelerated by an EDG, since both nucleofuges depart with the electrons originally bonded to the remainder of T^\pm .¹²⁻¹⁴ Thus, pK_a^0 has been concluded to be independent of the electronic nature of the substituent in the nonleaving group.¹²⁻¹⁴

We have recently reported that pyridinolysis of 2,4-dinitrophenyl benzoate (**1**) proceeds through a stepwise mechanism with a change in RDS at $pK_a^0 = 9.5$.^{7a} Our study has been extended to pyridinolysis of 2,4-dinitrophenyl phenyl carbonate (**2**) to investigate the effect of changing the Ph group in **1** by PhO (i.e., changing the substrate from **1** to **2**) on reactivity and mechanism including pK_a^0 . It is known that PhO is a stronger EWG than Ph on the basis of their σ_1 values (e.g., $\sigma_1 = 0.38$ for PhO and $\sigma_1 = 0.10$ for Ph),^{15a} while the former is also a stronger EDG than the latter on the basis of their σ_R values (e.g., $\sigma_R = -0.34$ for PhO and $\sigma_R = -0.11$ for Ph).^{15a} We wish to report that reactions of **2** result in a lower pK_a^0 than those of **1** by 1 pK_a unit although PhO behaves as a stronger EWG than Ph in the current reactions, and the k_2/k_{-1} ratio is independent of the nature of the nonleaving-group substituent.



Scheme 1



[†]This paper is dedicated with respect and affection to the late Professor Chi Sun Hahn, an inspiring teacher and mentor.

Table 1. Summary of second-order rate constants (k_N) for reactions of 2,4-dinitrophenyl benzoate (**1**) and 2,4-dinitrophenyl phenyl carbonate (**2**) with Z-substituted pyridines in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C^a

Z	pK _a	$k_N/M^{-1}s^{-1}$	
		1	2
1. 4-O ⁻	11.30	822 ± 7	8720 ± 390
2. 4-NMe ₂	9.12	43.0 ± 0.3	2630 ± 89
3. 4-NH ₂	8.93	32.0 ± 0.5	2520 ± 34
4. 3,4-Me ₂	5.78	(7.25 ± 0.04) × 10 ⁻²	17.4 ± 0.16
5. 4-Me	5.53	(4.69 ± 0.07) × 10 ⁻²	9.11 ± 0.14
6. 3-Me	5.09	(1.67 ± 0.02) × 10 ⁻²	3.83 ± 0.02
7. H	4.73	(8.61 ± 0.05) × 10 ⁻³	2.07 ± 0.03
8. 3-Cl	2.14	-	(1.40 ± 0.02) × 10 ⁻²

^aThe k_N values for the reactions of **1** were taken from ref. 7a.

Results and Discussion

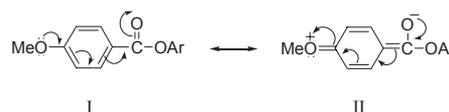
All reactions in this study obeyed pseudo-first-order kinetics in the presence of a large excess of pyridine. Pseudo-first-order rate constants (k_{obsd}) were determined from the equation $\ln(A_\infty - A_t) = -k_{\text{obsd}}t + C$. The correlation coefficient for the linear regression was usually higher than 0.9995. The plots of k_{obsd} vs. pyridine concentration were linear passing through the origin, indicating that the contribution of H₂O and/or OH⁻ ion from hydrolysis of pyridine to k_{obsd} is negligible. Thus, the second-order rate constants (k_N) were determined from the slope of the linear plots of k_{obsd} vs. [pyr] as shown in eq (1), in which [pyr] represents the concentration of pyridine. The uncertainty in the k_N values is estimated to be less than 3% from replicate runs. The k_N values determined in this study are summarized in Table 1 together with those reported previously for the corresponding reactions of **1** for comparison purpose.

$$k_{\text{obsd}} = k_N[\text{pyr}] \quad (1)$$

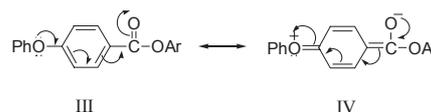
Effect of nonleaving group on reactivity. Table 1 shows that **2** is more reactive than **1**. It is noted that the reactivity difference becomes larger as the basicity of pyridine decreases, e.g., the reactivity ratio $k_N(\mathbf{2})/k_N(\mathbf{1})$ increases from ca. 10 to 80 and 240 as the pK_a of the conjugate acids of pyridines decreases from 11.30 to 8.93 and 4.73, in turn.

One can propose three plausible factors (e.g., steric, resonance, and inductive effects) to account for the reactivity difference. It is well known that rates of nucleophilic substitution reactions are strongly influenced by steric effect. The steric constant (E_S) of PhO is not available but is expected to be similar to that of PhCH₂ ($E_S = -0.38$).^{15b} Since the E_S value of Ph is -2.55,¹⁵ one can suggest that PhO is much less bulkier than Ph. Thus, the reduced steric effect might be attributed to the high reactivity of **2**. However, 4-nitrophenyl acetate has been reported to be less reactive than 4-nitrophenyl phenyl carbonate toward a series of primary amines,¹⁶ although CH₃ would exert less steric hindrance than PhO. Accordingly, other than steric effect is also responsible for the reactivity difference between **1** and **2**.

In nucleophilic substitution reactions of aryl X-substituted benzoates and related compounds, we found that substrates possessing an EDG in the nonleaving group exhibit lower reactivity than would be expected from the Hammett substituent constant.^{5,7,12-14} Since substrates possessing a π -electron donating group can be stabilized through resonance interactions as shown in resonance structures I and II, stabilization of the substrate has been concluded to be responsible for the decreased reactivity.^{5,7,12-14}



Since similar resonance structures are possible for **2** (but absent for **1**) as illustrated in resonance structures III and IV, one might expect that **2** is less reactive than **1**. However, the fact that **2** is more reactive than **1** indicates that the resonance effect cannot be significant in the current reactions. Thus, one can conclude that inductive effect is more significant than resonance effect in the present system (i.e., PhO behaves as a stronger EWG than Ph).



Reaction mechanism. To investigate the reaction mechanism, Brønsted-type plot for the reactions of **2** has been constructed together with the one for the corresponding reactions of **1** for comparison purpose. As shown in Figure 1, the plot for the reactions of **2** is nonlinear. Such a nonlinear Brønsted-type plot is typical for reactions reported to proceed through a stepwise mechanism with a change in RDS.¹⁻¹⁴ In fact, the nonlinear Brønsted-type plot for the reactions of **1** has been reported as evidence for a stepwise mechanism with a change in RDS.^{7a}

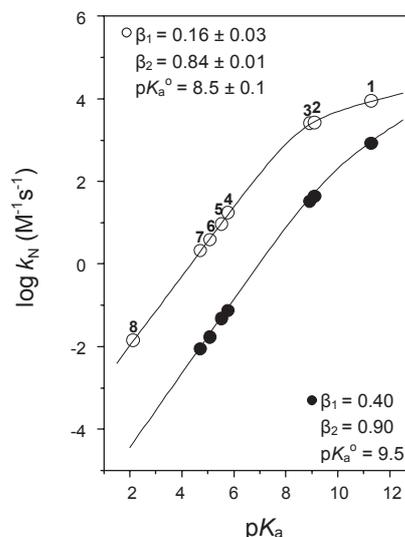


Figure 1. Brønsted plots for reactions of 2,4-dinitrophenyl benzoate **1** (●) and 2,4-dinitrophenyl phenyl carbonate **2** (○) with Z-substituted pyridines in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 1.

Thus, one can suggest that pyridinolysis of **2** proceeds also through a stepwise mechanism with a change in RDS upon changing the basicity of pyridines.

Figure 1 illustrates that the reactions of **2** result in a lower pK_a^0 than those of **1**, although **2** is more reactive than **1** (i.e., $pK_a^0 = 9.5$ for **1** and $pK_a^0 = 8.5$ for **2**). This is in contrast to the report that the substrate possessing an EWG in the nonleaving group is more reactive and results in a higher pK_a^0 than the substrate bearing an EDG.⁸ As illustrated in model V, Jencks *et al.* have suggested that an EWG in the nonleaving group pulls the non-bonding electrons in the oxygen atom of the leaving aryloxide. Since such pull and push would increase k_{-1} but decrease k_2 , it has been concluded that a decrease in the k_2/k_{-1} ratio is responsible for the increased pK_a^0 value observed for the reactions of substrates possessing an EWG in the nonleaving group.⁸



On the other hand, the push by the nonleaving group to accelerate expulsion of the leaving group from T^\ddagger is also possible as illustrated in model VI. Furthermore, PhO is a stronger EDG than Ph on the basis of their σ_R values. Thus, one might expect that the reactions of **2** would result in a larger k_2/k_{-1} ratio than the reactions of **1**. This appears to be consistent with the fact that the reactions of **2** result in a lower pK_a^0 than those of **1**. To examine this idea, the k_N values have been dissected into the microscopic rate constants (e.g., k_1 and k_2/k_{-1} ratios) in the following section.

Dissection of k_N into microscopic rate constants. The non-linear Brønsted-type plot for the reactions of **2** has been analyzed using a semiempirical equation (eq 2) reported by Castro¹⁷ and Jencks⁸ on the basis of the proposed mechanism shown in Scheme 1. The parameters β_1 and β_2 represent the slope of the curved Brønsted plots in Figure 1 for the reactions with strongly basic and weakly basic pyridines, respectively. Here k_N^0 refers to the k_N value at pK_a^0 where $k_2/k_{-1} = 1$. The parameters determined from the fitting of eq (2) to the experimental points are $\beta_1 = 0.16$, $\beta_2 = 0.84$ and $pK_a^0 = 8.5$ for the reactions of **2**, while the parameters reported previously for the corresponding reactions of **1** are $\beta_1 = 0.40$, $\beta_2 = 0.90$, and $pK_a^0 = 9.5$.

$$\log(k_N/k_N^0) = \beta_2(pK_a - pK_a^0) - \log(1 + \alpha)/2 \quad (2)$$

where $\log \alpha = (\beta_2 - \beta_1)(pK_a - pK_a^0)$

The apparent second-order rate constant k_N can be expressed as eq (3) by applying the steady-state conditions to the intermediate on the basis of the proposed mechanism. The k_2/k_{-1} ratios associated with the reactions of **2** have been determined using eqs (4) - (9) and the kinetic data in Table 1. Since eq (3) can be simplified to eq (4) or (5), β_1 and β_2 can be expressed as eqs (6) and (7), respectively.

$$k_N = k_1 k_2 / (k_{-1} + k_2) \quad (3)$$

$$k_N = k_1 k_2 / k_{-1}, \text{ when } k_2 \ll k_{-1} \quad (4)$$

$$k_N = k_1, \text{ when } k_2 \gg k_{-1} \quad (5)$$

$$\beta_1 = d(\log k_1) / d(pK_a) \quad (6)$$

$$\beta_2 = d(\log k_1 k_2 / k_{-1}) / d(pK_a) \\ = \beta_1 + d(\log k_2 / k_{-1}) / d(pK_a) \quad (7)$$

Eq (7) can be rearranged as eq (8). Integral of eq (8) from pK_a^0 to pK_a results in eq (9). Since $k_2 = k_{-1}$ at pK_a^0 , the term $(\log k_2 / k_{-1})_{pK_a^0}$ is zero. Therefore, one can calculate the k_2/k_{-1} ratios from eq (9) using $pK_a^0 = 8.5$, $\beta_1 = 0.16$, and $\beta_2 = 0.84$ for the reactions of **2**.

$$\beta_2 - \beta_1 = d(\log k_2 / k_{-1}) / d(pK_a) \quad (8)$$

$$(\log k_2 / k_{-1})_{pK_a} = (\beta_2 - \beta_1)(pK_a - pK_a^0) \quad (9)$$

The k_1 values have been determined from eq (10) using the k_N values in Table 1 and the k_2/k_{-1} ratios calculated above. The k_2/k_{-1} ratios and k_1 values for the reactions of **2** are summarized in Table 2. The corresponding values reported previously for the reactions of **1** are also given in Table 2 for comparison purpose.

$$k_N = k_1 k_2 / (k_{-1} + k_2) = k_1 / (k_{-1}/k_2 + 1) \quad (10)$$

As shown in Table 2, **2** exhibits larger k_1 values than **1** regardless of the pyridine basicity. In contrast, the magnitude of k_2/k_{-1} ratios is dependent on the basicity of pyridines, i.e., the reaction of **2** results in a larger k_2/k_{-1} ratio than that of **1** when $pK_a \geq 5.76$ but a smaller one when $pK_a \leq 5.32$. Thus, one can suggest that the higher reactivity shown by **2** is mainly due to its larger k_1 . Besides, the fact that **2** exhibits a larger k_1 than **1** supports the preceding conclusion that PhO behaves as a stronger EWG than Ph.

The effect of pyridine basicity on k_1 is illustrated in Figure 2. The Brønsted-type plot for the reactions of **2** exhibits excellent linear correlation with $\beta_1 = 0.16$. The plot for the corresponding reactions of **1** is also linear with $\beta_1 = 0.40$. It is generally under-

Table 2. Summary of microscopic rate constants (k_1 and k_2/k_{-1} ratio) for reactions of 2,4-dinitrophenyl benzoate (**1**) and 2,4-dinitrophenyl phenyl carbonate (**2**) with Z-substituted pyridines in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C^a

Z	pK_a	$k_N / M^{-1} s^{-1}$		k_2 / k_{-1}	
		1	2	1	2
1. 4-O ⁻	11.30	925	8830	7.94	80
2. 4-NMe ₂	9.12	109	3620	6.46×10^{-1}	2.64
3. 4-NH ₂	8.93	93.7	3810	5.19×10^{-1}	1.96
4. 3,4-Me ₂	5.78	5.32	1250	1.38×10^{-2}	1.41×10^{-2}
5. 4-Me	5.53	4.58	962	1.04×10^{-2}	9.60×10^{-3}
6. 3-Me	5.09	2.70	802	6.24×10^{-3}	4.80×10^{-3}
7. H	4.73	2.10	760	4.12×10^{-3}	2.73×10^{-3}
8. 3-Cl	2.14	-	306	-	4.73×10^{-5}

^aThe data for the reactions of **1** were taken from ref. 7a.

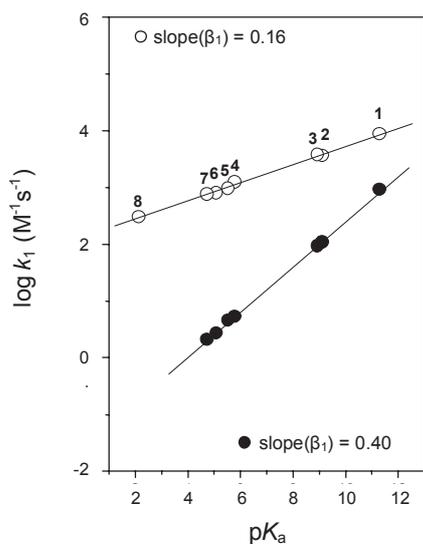


Figure 2. Plots for $\log k_1$ vs. pK_a for the pyridinolyses of 2,4-dinitrophenyl benzoate **1** (●) and 2,4-dinitrophenyl phenyl carbonate **2** (○) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 2.

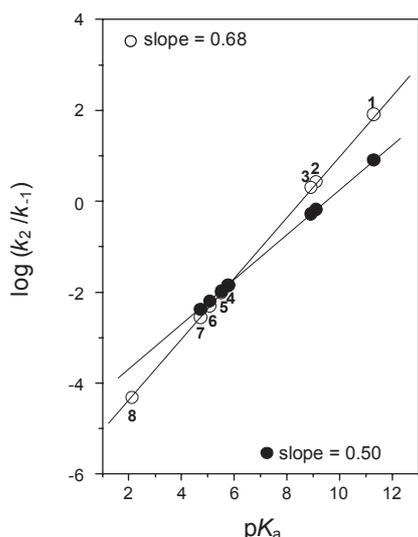


Figure 3. Plots for $\log k_2/k_{-1}$ vs. pK_a for the pyridinolyses of 2,4-dinitrophenyl benzoate **1** (●) and 2,4-dinitrophenyl phenyl carbonate **2** (○) in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 2.

stood that the magnitude of β_1 values represents a relative degree of bond formation between the nucleophile and the electrophile in the transition state.¹⁸ Thus, one can suggest that bond formation is much less advanced for the reactions of **2** than for those of **1**.

The effect of pyridine basicity on the k_2/k_{-1} ratio is illustrated in Figure 3. One can see that the k_2/k_{-1} ratio increases linearly as the pyridine basicity increases for the reactions of **1** and **2**, although the reaction of **2** exhibits a slightly larger slope than that of **1**. It is noted that the k_2/k_{-1} ratio is larger for the reaction of **2** than that of **1** when $pK_a \geq 5.78$ but smaller when $pK_a \leq 5.53$. Clearly, the k_2/k_{-1} ratio is independent of the nature of PhO and Ph. This is consistent with our previous proposal that the electronic nature of the substituent in the nonleaving group

does not influence the k_2/k_{-1} ratio.¹²⁻¹⁴ Furthermore, the reaction of **2** results in a lower pK_a^0 than that of **1**, although PhO behaves as a stronger EWG than Ph in the current study. This is in contrast to the report that an EWG increases pK_a^0 by decreasing the k_2/k_{-1} ratio,⁸⁻¹¹ but is consistent with our proposal that pK_a^0 is independent of the nature of the substituent in the nonleaving group.¹²⁻¹⁴

Conclusions

The current study has allowed us to conclude the following: (1) The reactions of **2** result in larger k_N and k_1 values than those of **1**. (2) PhO behaves as a stronger EWG than Ph, indicating that inductive effect is more significant than resonance effect for the current reactions. (3) The curved Brønsted-type plot for the reaction of **2** suggests that the reaction proceeds through a stepwise mechanism with a change in RDS. (4) The change of Ph in **1** by PhO does not affect the mechanism but decreases pK_a^0 from 9.5 to 8.5. (5) The k_2/k_{-1} ratio is independent of the electronic nature of the substituent in the nonleaving group.

Experimental

Materials. 2,4-Dinitrophenyl phenyl carbonate (**2**) was readily prepared from the reaction of phenyl chloroformate with 2,4-dinitrophenol in anhydrous ether under presence of triethylamine. Pyridines and other chemicals were of the highest quality available. Doubly glass distilled water was further boiled and cooled under nitrogen just before use. Due to low solubility of **2** in pure water, aqueous DMSO (80 mol % H₂O/20 ml % DMSO) was used as the reaction medium.

Kinetics. The kinetic study was performed using a UV-vis spectrophotometer for slow reactions (e.g., $t_{1/2} > 10$ s) or a stopped-flow spectrophotometer for fast reactions (e.g., $t_{1/2} < 10$ s) equipped with a constant temperature circulating bath to maintain the reaction mixture at 25.0 ± 0.1 °C. The reactions were followed by monitoring the appearance of 2,4-dinitrophenoxide. All the reactions were carried out under pseudo-first-order conditions in which pyridine concentrations were at least 20 times greater than the substrate concentration. The pyridine stock solution of ca. 0.2 M was prepared by dissolving 2 equiv. of pyridine and 1 equiv. of standardized HCl solution to make a self-buffered solution in a 25.0 mL volumetric flask except 3-chloropyridine.

Typically, the reaction was initiated by adding 5 μ L of a 0.02 M solution of **2** in acetonitrile to a 10-mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent and aliquot of the pyridine stock solution. All solutions were transferred by gas-tight syringes. Generally, the pyridine concentration was varied over the range (5 – 100) $\times 10^{-3}$ M, while the substrate concentration was ca. 4×10^{-5} M. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation, $\ln(A_\infty - A_t) = -k_{\text{obsd}}t + C$. The plots of $\ln(A_\infty - A_t)$ vs. time were linear over 90 % of the total reaction. Usually, five different pyridine concentrations were employed and replicate values of k_{obsd} were determined to obtain the second-order rate constants (k_N) from the slope of linear plots of k_{obsd} vs. pyridine concentrations.

Products analysis. 2,4-Dinitrophenoxide was liberated quantitatively and identified as one of the products in the reaction of **2** by comparison of the UV-vis spectrum after completion of the reaction with that of authentic sample under the same reaction condition.

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